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## SPECIFICATION

Magnesium Composite Powder, Its Manufacturing Method,  
Magnesium Group Composite Material and Its Manufacturing Method

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## TECHNICAL FIELD

The present invention relates to magnesium composite powder which is a starting raw material to manufacture a particle-dispersion type of magnesium group composite material by solid-phase reaction synthesis, its manufacturing method, a magnesium group composite material using the composite powder and its manufacturing method.

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## BACKGROUND ART

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A magnesium alloy is known as a most lightweight material and serves many uses. Meanwhile, the magnesium alloy has demerits such as low hardness, low rigidity, low abrasion resistance and low corrosion resistance.

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Therefore, conventionally, as a method to improve mechanical characteristics of the magnesium alloy, a particle-dispersion type of magnesium group composite material in which second-phase particles are dispersed in a matrix has been studied. Especially, research and development regarding a magnesium group composite material in which magnesium silicide ( $Mg_2Si$ ) particles having a light weight, high hardness, and high rigidity are dispersed has been increasingly focused on.

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For example, Japanese Unexamined Patent Publication No. 6-81068 discloses a manufacturing method of the magnesium group composite material in which magnesium silicide ( $Mg_2Si$ ) particles are dispersed. More specifically, when a magnesium alloy containing silicon (Si) in high concentration is injection molded in a semi-molten state, magnesium silicide ( $Mg_2Si$ ) is synthesized by a reaction of matrix magnesium (Mg) with silicon.

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In addition, Japanese Unexamined Patent Publication No.8-41564 discloses a magnesium group composite material in which magnesium silicide ( $Mg_2Si$ ) particles and silicon carbide (SiC) particles are dispersed by a casting method. In addition, Japanese Unexamined Patent Publication

No. 2000-17352 discloses a magnesium group composite material in which spherical magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles are dispersed by a casting method.

According to the related art disclosed in the above documents, the  
5 magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles which are dispersed in the magnesium group composite material are enlarged to  $100\mu\text{m}$  to several hundreds  $\mu\text{m}$  by particle growth in the course of being solidified from a molten state or a semi-molten state. As a result, a prominent increase in strength is not provided in the finally manufactured magnesium group composite material.  
10 Meanwhile, since the enlarged magnesium silicide particle causes a crack to be generated or spread, it lowers toughness of the material.

The inventor of the present invention applied for a patent for “magnesium group composite material, magnesium group composite material precursor and their manufacturing methods” as Japanese Patent  
15 Application No. 2001-292117 filed on September 25, 2001 and a patent for “magnesium group composite material, magnesium group composite material precursor and their manufacturing methods” as Japanese Patent Application No. 2001-292118 filed on September 25, 2001. These applications have not published yet at the moment. According to the  
20 inventions disclosed in these applications, a mixed solidified body in which silicon powder is finely grained is manufactured by performing a plasticity process on a mixture of a magnesium alloy in the form of powder or a chip and the silicon powder. Then, the mixed solidified body is heated to a temperature which is lower than a melting point ( $650^\circ\text{C}$ ) of magnesium,  
25 that is, in a solid-phase temperature range to react magnesium ( $\text{Mg}$ ) with silicon ( $\text{Si}$ ), so that fine magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles are uniformly dispersed in a matrix of the magnesium alloy. Thus, a new magnesium group composite material having excellent mechanical characteristics and abrasion resistance can be provided by the above solid-phase synthesizing  
30 process.

According to the magnesium group composite material in which the fine magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles are uniformly dispersed using the solid-phase reaction synthesizing method between magnesium ( $\text{Mg}$ ) and

silicon (Si), since the silicon particle in the mixed solidified body before the reaction is not prominently enlarged by particle growth in the course of the solid-phase reaction, the size of the silicon (Si) before the reaction almost coincides with that of the magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particle. Therefore, the magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particle in the magnesium group composite material is miniaturized by finely dispersing the silicon particles in the mixed solidified body, so that high strength and high performance of the composite material can be implemented.

When the hard particles such as magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles are finely and uniformly dispersed in a matrix of the magnesium alloy, characteristics of the magnesium group composite material are improved. Thus, when appropriate plasticity processes are repeatedly performed to the mixture of the magnesium alloy starting raw material and the silicon powder, the silicon particle can be miniaturized and dispersed. However, in view of further implementing low cost of the alloy material, the plasticity process is preferably omitted.

As a method of miniaturizing the silicon particle instead of the plasticity process, it is thought that fine silicon powder is used as the starting raw material. When fine powder having a diameter of about  $1\mu\text{m}$  is used as the starting raw material, the size of the magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particle generated by the solid-phase reaction synthesis becomes almost  $1\mu\text{m}$ .

Regarding the size of the magnesium (Mg) alloy material which is the other starting material, when the size of the magnesium alloy powder or the magnesium alloy chip becomes considerably large as compared with that of the silicon (Si) particle, two layers are separated, that is, only the fine silicon particles are segregated in one part in the mixture of the magnesium alloy starting raw material and the silicon particles. In order to avoid the above problem, it is thought that fine magnesium alloy material is used as the starting raw material. However, since magnesium has active characteristics in which it is likely to be oxidized, fine magnesium alloy powder having a diameter of several tens  $\mu\text{m}$  could be exploded in the air.

In view of such danger, it is very difficult to use the fine magnesium alloy powder as the starting material in practice.

As described above, there are following problems when the fine silicon particles are used as the starting raw material, that is,

- 5      1)      segregation of the magnesium silicide ( $\text{Mg}_2\text{Si}$ ) particles in the magnesium group composite material, and
- 2)      treatment of the powder in a manufacturing process.

#### DISCLOSURE OF THE INVENTION

10          The present invention was made to solve the above problems and it is an object of the present invention to provide a magnesium group composite material in which compound particles generated by a solid-phase reaction with magnesium which is a main component are uniformly dispersed in a matrix of the magnesium alloy.

15          It is another object of the present invention to provide a magnesium composite powder as a starting raw material to manufacture the above magnesium group composite material.

            It is still another object of the present invention to provide a method of manufacturing the above magnesium group composite material with high  
20      economical efficiency.

            It is still another object of the present invention to provide a method of manufacturing the magnesium composite powder as the starting raw material for the above magnesium group composite material with high efficiency.

25          When the magnesium alloy material such as powder or a chip is used as the starting raw material, in view of avoiding explosion in the air, its size is preferably about  $500\mu\text{m}$  to  $5\text{mm}$ . Meanwhile, the size of the fine-grained powder comprising a component which reacts with magnesium to form the compound is about  $0.5\mu\text{m}$  to  $50\mu\text{m}$ .

30          According to the present invention, the fine-grained powder is attached on a surface of the magnesium alloy coarse particle which is the main component. As the particle diameter of the fine-grained powder is about 1/10 to 1/1000 of the magnesium alloy coarse particle, the

fine-grained powder is considerably fine as compared with the magnesium alloy coarse particle. While the magnesium composite powder in which the fine-grained powder is attached on the surface of the magnesium alloy coarse particle is pressed, solidified and heated, compound particles are formed by a solid-phase reaction synthesis in the course of heating the solidified body. According to the present invention, the magnesium group composite material having superior characteristics is manufactured with high economical efficiency by dispersing the above compound particles in the matrix.

The inventor of the present invention resulted in providing the magnesium group composite material having high mechanical characteristics such as high strength, high hardness, and high rigidity, superior abrasion resistance and low friction coefficient at the time of frictional sliding through various kinds of experiments and studies.

Magnesium composite powder according to the present invention is a starting raw material to manufacture a particle-dispersion type of magnesium group composite material by a solid-phase reaction synthesis. The magnesium composite powder comprises magnesium alloy coarse particles serving as a main component which constitutes a matrix of a magnesium alloy and fine-grained powder comprising a component which reacts with magnesium to form a compound, and attached on a surface of the magnesium alloy coarse particle.

It is preferable that the fine-grained powder attached on the surface of the magnesium alloy coarse particle comprises at least one kind of powder particle selected from a group comprising silicon (Si), silica ( $\text{SiO}_2$ ),  $\gamma$  alumina ( $\text{Al}_2\text{O}_3$ ) and aluminum (Al).

Preferably, a particle diameter of the magnesium alloy coarse particle is 100 $\mu\text{m}$  to 5mm and a particle diameter of the fine-grained powder is not more than 100 $\mu\text{m}$ . More preferably, a particle diameter of the magnesium

alloy coarse particle is 500 $\mu\text{m}$  to 2mm and a particle diameter of the

fine-grained powder is 0.5 $\mu$ m to 50 $\mu$ m.

According to one embodiment, the fine-grained powder is attached on the surface of the magnesium alloy coarse particle through a binder. According to another embodiment, the fine-grained powder and the magnesium alloy coarse particle are mechanically bonded. According to still another embodiment, the fine-grained powder is attached on the surface of the magnesium alloy coarse particle through oil.

A magnesium group composite material according to the present invention is manufactured using the above magnesium composite powder in which reaction products of the magnesium alloy coarse particle and the fine-grained powder are dispersed in a matrix of a magnesium alloy. The reaction product preferably comprises at least one kind of compound selected from a group consisting of Mg<sub>2</sub>Si, MgO, Al<sub>3</sub>Mg<sub>2</sub>, Mg<sub>17</sub>Al<sub>12</sub> and MgAl<sub>2</sub>O<sub>4</sub>.

When a friction coefficient is to be lowered, the magnesium group composite material preferably comprises graphite powder as a solid lubricant agent and it is desirable that 0.5% to 3% by weight of the graphite powder is contained in the magnesium group composite material.

In addition, preferably, 20% or less by weight of the reaction products is contained in the magnesium alloy matrix. More preferably, 5% to 10% by weight of the reaction products is contained.

A manufacturing method of the magnesium composite powder according to the present invention comprises the following steps, that is,

- a) a step of preparing magnesium alloy coarse particles,
- b) a step of mixing fine-grained powder comprising a component which reacts with magnesium to form a compound, in a binder solution, and
- c) a step of spraying the binder solution containing the fine-grained powder onto the magnesium alloy coarse particles and drying it.

A manufacturing method of a magnesium composite powder according to the present invention comprises the following steps, that is,

- a) a step of attaching fine-grained powder comprising a compound which reacts with magnesium to form a compound, on a surface of a magnesium alloy coarse particle,
- b) a step of pressing and solidifying magnesium composite powder in which

the fine-grained powder is attached on the surface of the magnesium alloy coarse particle,

c) a step of heating a solidified body provided by the pressing and solidifying step in an inert gas atmosphere or a non-oxidizing gas atmosphere, and generating compound particles by solid-phase reaction synthesis of the magnesium alloy coarse particle and the fine-grained powder, and

d) a step of densifying the solidified body by performing a warm plasticity process on the solidified body which generated the compound particles.

Preferably, the warm plasticity process is an extrusion method in which an extrusion ratio is not less than 20. More preferably, the extrusion ratio of the extrusion method is not less than 35.

Preferably, the compound particle comprises at least one kind of compound selected from a group consisting of  $\text{Mg}_2\text{Si}$ ,  $\text{MgO}$ ,  $\text{Al}_3\text{Mg}_2$ ,  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{MgAl}_2\text{O}_4$ .

According to one embodiment, the fine-grained powder is attached on the surface of the magnesium alloy coarse particle using a binder. In this case, preferably, the step of attaching the fine-grained powder comprises a step of mixing the fine-grained powder in a binder solution, and a step of spraying the binder solution containing the fine-grained powder on the magnesium alloy coarse particle and drying it.

According to another embodiment, the fine-grained powder is attached on the surface of the magnesium alloy coarse particle using oil. Regarding the characteristics of the oil to be used, an evaporation temperature of the oil is not more than  $400^\circ\text{C}$  in an inert gas atmosphere or a non-oxidizing atmosphere, for example.

The oil is attached as follows, for example. First, the magnesium alloy coarse particle powder is charged in a container. Then, the oil is put in the container and it is uniformly attached on the surface of the magnesium alloy coarse particle powder by rotating, shaking and oscillating the container. Then, the fine-grained powder is put in the container and attached on the surface of the magnesium alloy coarse particle powder through the oil by rotating, shaking and oscillating the container again.

Preferably, 0.2 to 1% by weight, more preferably 0.3 to 0.6% by weight

of the oil is added in the magnesium alloy coarse particle powder.

The oil may be attached as follows. First, the magnesium alloy coarse particle powder is charged in a container. Then, the oil and balls are put in the container and uniformly attached on the surface of the magnesium alloy coarse particle powder by rotating, shaking and oscillating the container. Then, the fine-grained powder is put in the container and attached on the surface of the magnesium alloy coarse particle powder through the oil by rotating, shaking and oscillating the container again.

According to still another embodiment, the fine-grained powder is mechanically bonded to the surface of the magnesium alloy coarse particle.

### BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is an illustrative view showing one example of a method of attaching fine-grained powder on a surface of a magnesium alloy coarse particle using a binder;

Fig. 2 is an illustrative view showing another example of the method of attaching fine-grained powder on the surface of the magnesium alloy coarse particle using the binder;

Fig. 3 is an illustrative view showing still another example of the method of attaching fine-grained powder on the surface of the magnesium alloy coarse particle using the binder;

Fig. 4 is an illustrative view showing one example of magnesium composite powder in which the fine-grained powder is attached on the surface of the magnesium alloy coarse particle;

Fig. 5 is an illustrative view showing one example of a method of mechanically bonding the fine-grained powder onto the surface of the magnesium alloy coarse particle;

Fig. 6 is an illustrative view showing another example of the method of mechanically bonding the fine-grained powder onto the surface of the magnesium alloy coarse particle;

Fig. 7 is an illustrative view showing still another example of the method of mechanically bonding the fine-grained powder onto the surface of the magnesium alloy coarse particle;

Fig. 8 is an illustrative view showing another example of the magnesium composite powder in which the fine-grained powder is attached



on the surface of the magnesium alloy coarse particle;

Fig. 9 is a view showing one example of a manufacturing method of a magnesium group composite material;

Fig. 10 is a view showing another example of the manufacturing method of the magnesium group composite material;

Fig. 11 is a view illustratively showing a composition of a pressed powder solidified body before a solid-phase reaction;

Fig. 12 is a view illustratively showing a composition of a magnesium alloy after the solid-phase reaction;

Fig. 13 is a microscope photograph showing a composition of the magnesium composite powder in which silica powder is mechanically bonded onto an AZ91 surface;

Fig. 14 is a view showing a method of simply evaluating an attached state of silicon powder; and

Fig. 15 is a view showing an evaluated result of the attached states of the silicon powder.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Characteristics and an effect of the present invention will be described hereinafter.

##### (1) Magnesium composite powder

Magnesium composite powder is a starting material to manufacture a particle-dispersion type of magnesium group composite material and it comprises magnesium alloy coarse particles and fine-grained powder attached on a surface of the magnesium alloy coarse particles.

##### (A) Magnesium alloy coarse particle

The term "coarse particle" used in this specification includes a particle in the form of a chip and a particle in the form of a lump other than powder. The chip-shaped magnesium alloy coarse particles are provided by cutting a magnesium alloy billet (ingot). The lump-shaped particles are provided by acquiring a large lump from an ingot by a grinding machine and mixing and grinding it by a ball mill and the like.

Since magnesium is an active material, fine magnesium alloy powder could be exploded by an oxidation reaction in the air. In order to avoid such danger, a particle diameter of the magnesium alloy coarse particle is

preferably about 100 $\mu$ m to 5mm. More preferably, it is 500 $\mu$ m to 2mm.

When the particle diameter of the magnesium alloy coarse particle is below 100 $\mu$ m, it is highly likely that a dust explosion is caused in the course of

treatment. Meanwhile, if the particle diameter of the magnesium alloy coarse particle is more than 5mm, when the provided magnesium composite powder is pressed and solidified, a crack could be generated on a surface or at a corner part of the solidified body, so that a preferable solidified body cannot be provided. Thus, the magnesium alloy coarse particles provided by the above manufacturing method, which pass through a mesh of 5mm

but do not pass through a mesh of 100 $\mu$ m in a shifting method are used as a raw material.

As described above, the magnesium alloy coarse particle includes the powder particle, the chip-shaped particle and the lump-shaped particle. The term "particle diameter" in those several kinds of particles means a maximum length in each of the above various shapes. The particle diameter is measured by direct observation using a stereo microscope, an optical microscope, and a scanning electron microscope, or measured using a magnification projector or a particle size distribution measuring machine which is used in measuring a powder particle diameter.

The magnesium alloy coarse particles form a matrix of the magnesium group composite material and as its alloy component, an existing magnesium alloy such as AZ31 (Mg-3%Al-1%Zn/percentage by weight) or AZ91 (Mg-9%Al-1%Zn/ percentage by weight) may be used, for example. However, the alloy component is not particularly limited.

#### (B) Fine-grained powder

The fine-grained powder attached on the surface of the magnesium alloy coarse particle generates compound particles by a solid-phase reaction synthesis with magnesium. As such fine-grained powder, at least one kind of powder selected from a group comprising silicon (Si), silica (SiO<sub>2</sub>),  $\gamma$  alumina (Al<sub>2</sub>O<sub>3</sub>) and aluminum (Al) is used.

The following compound particles are generated by the solid-phase

reaction synthesis using the above fine-grained powder. That is, when silicon powder is used,  $\text{Mg}_2\text{Si}$  is provided. When silica powder is used,  $\text{Mg}_2\text{Si}$  and  $\text{MgO}$  are provided. When  $\gamma$ alumina is used,  $\text{Al}_3\text{Mg}_2$  and/or  $\text{Mg}_{17}\text{Al}_{12}$  and/or  $\text{MgAl}_2\text{O}_4$  are provided in addition to  $\text{MgO}$ . When aluminum is used,  $\text{Al}_3\text{Mg}_2$  and/or  $\text{Mg}_{17}\text{Al}_{12}$  are provided.

In addition, although alumina has two kinds of crystal structures such as  $\gamma$  and  $\alpha$ , the inventor of the present invention found that only  $\gamma$ alumina could generate the above compound particles by the reaction with magnesium. Since  $\alpha$ alumina is stable as compared with  $\gamma$ alumina, it was confirmed that it could not react with the magnesium alloy in a range of a solid-phase temperature of  $650^\circ\text{C}$  or less. Therefore, the alumina fine-grained powder attached on the magnesium alloy coarse particle surface needs to have the  $\gamma$ crystal structure.

A preferable particle diameter of respective fine-grained powder is  $0.5\text{ }\mu\text{m}$  to  $100\text{ }\mu\text{m}$ . Since the fine-grained powder reacts with magnesium in the solid-phase temperature range, the particle diameter of the generated compound particle almost coincides with the particle diameter of the fine-grained powder before the reaction. In order to improve characteristics such as strength, hardness, abrasion resistance of the magnesium group composite material, the smaller the particle diameter of the compound particle dispersed in the matrix becomes, the more preferable it is. Therefore, it is desirable that the particle diameter of the fine-grained powder selected from silicon ( $\text{Si}$ ), silica ( $\text{SiO}_2$ ),  $\gamma$ alumina ( $\text{Al}_2\text{O}_3$ ) and aluminum ( $\text{Al}$ ) used as the raw material is small. When the diameter of the fine-grained powder is more than  $100\text{ }\mu\text{m}$ , the characteristics of the magnesium group composite material is lowered. Meanwhile, when

the particle diameter of the fine-grained powder is below  $0.5\mu\text{m}$ , the fine-grained powder strongly agglutinate with each other by an influence such as electrostatic attraction among fine-grained powder or surface adsorption water, and coarse powder having a particle diameter of more than  $100\mu\text{m}$  is generated. As a result, since the compound particle dispersed in the matrix of the magnesium group composite material has a particle diameter more than  $100\mu\text{m}$ , its characteristics are lowered.

Especially, in order to keep high toughness which is one of the superior characteristics of the magnesium alloy and to provide high strength, it is preferable that the particle diameter of the dispersed compound particle is not more than  $50\mu\text{m}$ . In order to improve the toughness as well as strength and hardness of the magnesium group composite material, it is preferable that the particle diameter of the fine-grained powder is  $0.5\mu\text{m}$  to  $10\mu\text{m}$ . The particle diameter of the fine-grained powder is measured by using a method of transmitting light while the powder is stirred and dispersed in a glycol or water solution and measuring particle size distribution from a degree of light transmission.

(C) Composing of magnesium alloy coarse particles and fine-grained powder

The magnesium composite powder is provided by uniformly dispersing and attaching the fine-grained powder to the surface of the magnesium alloy coarse particle. Thus, the above composite powder is used as the starting raw material and when pressing and solidifying, heating and warm plasticity process are performed on the composite powder, the magnesium group composite material in which fine compound particles are uniformly dispersed in the matrix can be provided.

A method of uniformly dispersing and attaching the fine-grained powder on the surface of the magnesium alloy coarse particle includes a method of bonding both of them through a binder, a method of bonding both

of them through oil, and a method of mechanically bonding both of them by applying external force.

In the case of the bonding method through the binder, the binder is preferably soluble in water or an organic solvent and selected from water-soluble dextran, a sugar group, a cellulose group, and a synthetic polymer. As the water-soluble binder, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polyvinyl methyl ether (PVM), polyacrylamide, methylcellulose (MC), starch and the like can be used. As the binder which is soluble in the organic solvent, polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG), hydroxypropylcellulose (HPC), hydroxypropyl methylcellulose, ethylcellulose (EC), acetylcellulose and the like can be used.

Figs. 1 to 3 show examples of the bonding methods through the binder by a wet granulating machine or a spray drier.

According to the method shown in Fig. 1, a mixture 2 of the magnesium alloy coarse particles and the fine-grained powder are charged in a container 1 and warm wind 3 is supplied from a lower part of the container 1 to suspend the mixture 2. In this state, the binder is applied to the surface of the particle by spraying a binder solution 4 to the mixture 2 from above, and the mixture is dried at high temperature at the same time. As a result, as shown in Fig. 4, fine-grained powder 8 is bonded to a surface of a magnesium alloy coarse particle 7 through the binder 9.

According to the method shown in Fig. 2, in a state where the mixture 2 of the magnesium alloy coarse particles and the fine-grained powder is suspended in the container 1, a binder solution is sprayed at the lower part in a direction perpendicular to wind direction.

According to the method shown in Fig. 3, only magnesium alloy coarse particles 5 are charged into the container 1 and the coarse particles are suspended by supplying warm wind from the lower part of the container. A binder solution 6 to be sprayed toward the magnesium alloy coarse particles 5 contains fine-grained powder. While the binder solution 6 is sufficiently stirred to prevent the fine-grained powder from being precipitated in the binder solution 6, the binder solution 6 is sprayed to the magnesium alloy coarse particles 5 from an upper part of the container 1. In addition, the binder solution 6 may be sprayed at the lower part as shown in Fig. 2. According to this method, the fine-grained powder can be uniformly

attached on the surface of the magnesium alloy coarse particle. Since the fine-grained powder is considerably smaller than the magnesium alloy coarse particle, when the mixture of those is suspended by strong wind, the fine-grained powder tends to go above the coarse particles in a granulating machine (container). The reason for this is thought that a specific surface area of the fine-grained powder is larger than that of the coarse particle. Therefore, a separation phenomenon between the fine-grained powder and the magnesium coarse particle in the granulating machine could be generated and in this case, it takes time to uniformly attach the fine-grained powder on the surface of the magnesium alloy coarse particle. In order to avoid such problem, it is effective to mix the fine-grained powder in the binder solution previously.

As a medium to attach the fine-grained powder on the surface of the magnesium alloy coarse particle, oleic oil may be used instead of the binder. More specifically, predetermined magnesium composite powder is provided by attaching oil such as the oleic oil on the magnesium alloy coarse particle and then mixing the fine-grained powder to it by a ball mill and the like.

Regarding the characteristics of the oil to be used, an evaporation temperature of the oil in an inert gas atmosphere or a non-oxidizing atmosphere is not more than 400°C, for example.

Concretely, the oil is attached as follows, for example. First, the magnesium alloy coarse particles are charged into the container. Then, the oil is poured in the container and the container is rotated, shaken and oscillated to uniformly attach the oil on the surface of the magnesium alloy coarse particle. Then, the fine-grained powder is charged into the container and the container is rotated, shaken and oscillated again to attach the fine-grained powder on the surface of the magnesium alloy coarse particle through the oil.

An amount of the oil is preferably 0.2 to 1% by weight in the magnesium alloy coarse particle powder and more preferably, it is 0.3 to 0.6% by weight. When the amount of the oil is less than 0.2% by weight, the most part of the fine-grained powder is separated from the surface of the magnesium alloy coarse particle without being attached on it. Meanwhile, even when the oil is added beyond 1% by weight, its attachment effect is not

improved and the oil is left in the magnesium group composite material even if the heat treatment is performed in the post-process, so that its strength or breaking elongation is lowered. Thus, more preferably, the amount of the oil is 0.3 to 0.6% by weight. When the added amount is not less than 0.3% by weight, separation of the fine-grained powder is not generated at all and the fine-grained powder can be completely attached on the surface of the coarse particle powder. When the added amount is not more than 0.6%, the oil is not left in the magnesium group composite material, and a heat treatment time needed to dissolve and remove the oil can be shortened, which is preferable in view of economical efficiency.

The structure of the magnesium composite powder provided as described above is substantially the same as that shown in Fig. 4. The oil is left instead of the binder 9.

Figs. 5 to 7 show methods of mechanically bonding the fine-grained powder onto the surface of the magnesium alloy coarse particle.

According to the method shown in Fig. 5, the mixture 2 of the magnesium alloy coarse particles and the fine-grained powder are put into a machine called a roller compactor 10. Granules 14 in which the fine-grained powder is mechanically bonded and attached on the surface of the magnesium alloy coarse particle are provided by pressing the mixture 2 at an engaging part of a pair of toothed wheels 11 and 12. Magnesium composite powder 15 having a predetermined dimension and configuration can be provided by passing the granules 14 through a grinding and shifting machine 13. As shown in the magnesium composite powder 15 shown in Fig. 8, the fine-grained powder 8 is mechanically bonded and attached on the surface of the magnesium alloy coarse particle 7.

According to the method using a vertical type of roller compactor 20 shown in Fig. 6, a pair of cylindrical rollers 16 and 17 is used instead of the pair of toothed wheels. In addition, according to the method using a lateral type of roller compactor 30 shown in Fig. 7, the mixture of the magnesium alloy coarse particles and the fine-grained powder is conveyed to a pair of cylindrical rollers 16 and 17 by a belt conveyer 18. The mixture may be laterally supplied by a screw feeder instead of using the belt conveyer.

The machine used to mechanically bond and attach the fine-grained powder on the surface of the magnesium alloy coarse particle is not limited

to the roller compactor. For example, the magnesium composite powder in which the fine-grained powder is mechanically bonded on the coarse particle surface can be provided by using a ball mill or a rolling machine.

(2) Addition of graphite powder as solid lubricant agent

When it is desired to reduce a friction coefficient at the time of frictional sliding in the magnesium group composite material, it is preferable to add and disperse graphite powder serving as a solid lubricant agent together with the magnesium composite powder in the magnesium group composite material. As a kind of the graphite powder, both natural graphite and artificial graphite may be used. Its configuration is also not particularly limited and spherical or flake graphite powder may be used.

An added amount of the graphite powder is preferably 0.5 to 3% by weight as an external addition in an entire magnesium group composite material. When it is below 0.5%, a reducing effect of the friction coefficient is not provided. Meanwhile, when it is more than 3%, the strength of the magnesium group composite material is considerably lowered.

In addition, similar to the above fine-grained powder, the graphite powder may be attached and bonded on the surface of the magnesium alloy coarse particle to be mixed and added.

(3) Magnesium group composite material

The magnesium group composite material is provided by pressing and solidifying the above magnesium composite powder and then heating and maintaining the solidified body in a predetermined temperature range. While the solidified body is heated and maintained in the predetermined temperature range, solid-phase reaction synthesis including an oxidation-reduction reaction is progressed between a magnesium component of the magnesium alloy coarse particle and the fine-grained powder attached and bonded onto the coarse particle surface, which constitute the magnesium composite powder, and thus provided compound particles are uniformly dispersed in a matrix.

The compound particles generated by the solid-phase reaction comprise at least one kind of compound selected from a group comprising  $\text{Mg}_2\text{Si}$ ,  $\text{MgO}$ ,  $\text{Al}_3\text{Mg}_2$ ,  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{MgAl}_2\text{O}_4$ . Among them,  $\text{Mg}_2\text{Si}$ ,  $\text{Al}_3\text{Mg}_2$ ,  $\text{Mg}_{17}\text{Al}_{12}$  have an effect to improve the strength, hardness, abrasion resistance of the magnesium alloy. Especially, since  $\text{Mg}_2\text{Si}$  has high



rigidity as compared with the other compound particles, when it is dispersed in the matrix of the magnesium group composite material, rigidity of the composite material is improved. Since oxides such as MgO and  $\text{MgAl}_2\text{O}_4$  have low hardness as compared with other compound particles, there is an effect to reduce opponent aggressiveness. As a result, when it is dispersed in the matrix of the composite material, the friction coefficient at the time of frictional sliding is reduced.

It is preferable that a total content of the compound particles in the magnesium group composite material is not more than 20% by weight. When the total content is more than 20%, the toughness of the magnesium group composite material is considerably lowered. A more preferable range of the total content is 5 to 10%. As long as the range is satisfied, the magnesium group composite material having superior strength and toughness can be provided.

#### (4) Manufacturing method of magnesium group composite material

Figs. 9 and 10 show steps of manufacturing methods of the magnesium group composite material. A difference between the manufacturing methods shown in Figs. 9 and 10 is in a step of manufacturing the magnesium composite powder. According to the method shown in Fig. 9, the magnesium alloy coarse particles and the fine-grained powder are weighed and mixed and then both are attached and bonded. According to the method shown in Fig. 10, the fine-grained powder is previously mixed in the binder solution and the mixture solution containing the fine-grained powder is sprayed to the magnesium alloy coarse particles, so that both are attached and bonded.

##### (A) Manufacturing of magnesium composite powder

As described above, the method of attaching and bonding the fine-grained powder onto the surface of the magnesium alloy coarse particle may include the method using the binder, the method using the oil, the method of mechanically bonding them by applying external force and the like. By the above methods, the magnesium composite powder in which the fine-grained powder is dispersed and attached and bonded to the surface of the magnesium alloy coarse particles can be provided.

##### (B) Pressing and solidifying of magnesium composite powder

A method of pressing and solidifying the magnesium composite powder

includes a press molding solidification method or a cold isostatic press (CIP) solidification method which is used in a normal powder metallurgical method. Especially, when a large pressed powder molded material having a diameter beyond 100mm is manufactured, the cold isostatic press solidification method is preferably used. A relative density of the pressed powder solidified body is preferably 80% or more. When the relative density is below 80%, the strength of the pressed powder solidified body is lowered, so that it could be damaged or cracked or become defective in the course of transportation.

Fig. 11 illustrates a composition of the pressed powder solidified body before the solid-phase reaction. As shown in the drawing, fine-grained powder 41 is uniformly dispersed in a magnesium alloy matrix 40.

(C) Generation of compound particles by heating the pressed powder solidified body

The solid-phase reaction synthesis including the oxidation-reduction reaction is progressed between the magnesium alloy coarse particle and the fine-grained powder in the course of heating and holding the pressed powder solidified body, so that composite particle comprising  $Mg_2Si$ ,  $MgO$ ,  $Al_3Mg_2$ ,  $Mg_{17}Al_{12}$  or  $MgAl_2O_4$  is generated. As shown in Fig. 12, reaction products 42 and reaction products 43 and the like are dispersed in the magnesium alloy matrix 40.

When the magnesium alloy coarse particle surface reacts (oxides) with oxygen in an atmosphere in the heating process, a magnesium oxide film is formed on the surface. The oxide film hinders a reaction between the magnesium alloy coarse particle and the fine-grained powder. Therefore, in view of preventing the oxidization, the atmosphere to heat the pressed powder solidified body is preferably an inert gas atmosphere or a non-oxidizing atmosphere.

Regarding a heating temperature, it varies depending on the kind of the fine-grained powder to be combined. Since heat is generated at the time of solid-phase reaction with the magnesium alloy coarse particle even if any fine-grained powder is used, a reaction start temperature and a reaction end temperature can be correctly known using a differential calorie analyzing apparatus. Therefore, the compound particles can be finely generated by setting the heating and holding temperature of the pressed

powder solidified body at the reaction end temperature found by the differential calorie analyzing apparatus. In addition, since the present invention is characterized by preventing the compound particle generated using the solid-phase reaction at a temperature below a melting point of magnesium from becoming large and growing, a maximum heating temperature is less than 650°C.

When the pressed powder solidified body of the magnesium composite powder manufactured using the oil is heated in the inert gas atmosphere or the non-oxidizing atmosphere, the oil is dissolved and evaporated to be removed from the pressed powder solidified body. At this time, when the evaporation temperature of the oil is more than 400°C, the oil remains in the pressed powder solidified body, so that the strength or breaking elongation is lowered. Therefore, regarding the oil used in attaching the fine-grained powder, its evaporation temperature in the inert gas atmosphere or the non-oxidizing atmosphere is preferably not more than 400°C.

#### (D) Warm plasticity processing

In order to obtain sufficient mechanical characteristics in the magnesium group composite material, it is preferable that its relative density is not less than 98%. Since the relative density of the pressed powder solidified body is 80% to 90% in general, the warm plasticity processing is performed to densify it after the above heating process in the present invention. The warm plasticity processing method may include an extruding method, a forging method, a rolling method and the like. Among them, the warm extruding method is suitable for manufacturing a rod-shaped or pipe-shaped magnesium alloy material. In order to densify the pressed powder solidified body, it is preferable that an extrusion ratio is to be not less than 20. When the extrusion ratio is 35 or more especially, the compound particles generated by the solid-phase reaction synthesis are more finely ground so that they can be more uniformly dispersed in the matrix of the magnesium group composite material.

As described above, according to the present invention, there can be

provided a magnesium group composite material having mechanical characteristics such as high strength, high hardness and high toughness, and superior frictional sliding characteristics. Especially, there can be provided a magnesium group composite material which can implement a small friction coefficient. Since such magnesium group composite material provides a light weight effect in addition to the above characteristics, it can be applied to a component for an automobile, a bicycle, a bike, a mechanical component, a structural component, an industrial robot arm, a medical instrument, a nursing-care assistance device, a baby carriage component and the like.

(1) Working example 1

As a starting raw material to constitute a matrix to manufacture the magnesium alloy, AZ31 magnesium alloy coarse particle powder having a maximum particle diameter of 1.5mm, a minimum particle diameter of 550  $\mu\text{m}$  and an average particle diameter of 870 $\mu\text{m}$  was prepared. Meanwhile, as the added powder, fine-grained powder of silicon (Si), silica ( $\text{SiO}_2$ ),  $\gamma$  alumina ( $\text{Al}_2\text{O}_3$ ) and aluminum (Al) were prepared. Particle diameters (maximum, average, minimum) of the above powder measured by laser diffraction and scattering method are shown in a table 1.

[Table 1]

Fine-grained powder	Silicon (Si)	Silica ( $\text{SiO}_2$ )	$\gamma$ alumina ( $\text{Al}_2\text{O}_3$ )	Aluminum (Al)
Maximum value ( $\mu\text{m}$ )	55	48	38	44
Average value ( $\mu\text{m}$ )	22	20	14	23
Minimum value ( $\mu\text{m}$ )	4	3	5	9

The AZ31 coarse particle powder and each fine-grained powder were weighed and mixed so that 5% by weight of the fine-grained powder might be contained. As a binder solution, PVA (polyvinyl alcohol) water solution having a concentration of 2% was prepared.

Each mixed powder was put in a wet granulating apparatus and in a state where the mixed powder was suspended and stirred by warm wind

(kept at 75°C) from the lower part of the apparatus and a moving vane provided at the bottom of the apparatus, and the PVA water solution was sprayed from a spray gun set at the upper part or the lower part of the apparatus. Thus, there was provided a magnesium composite granulated powder in which each fine-grained powder was attached on the surface of the AZ31 coarse particle powder using the PVA binder as a glue.

Appearance result of attached states of the fine-grained powder on the surface of the AZ31 coarse particle powder provided under varied sprayed amounts of the PVA water solution to the whole mixture powder is shown in a table 2.

[Table 2]

No.	Fine-grained powder	Sprayed position	PVA water solution (%)	PVA solid quantity (%)	Attached state of fine-grained powder
1	Silicon	Upper part	20%	0.4%	Good
2	Silica	Lower part	20%	0.4%	Good
3	yalumina	Upper part	20%	0.4%	Good
4	Aluminum	Lower part	20%	0.4%	Good
5	Silicon	Upper part	40%	0.8%	Good
6	Silicon	Upper part	10%	0.2%	Good
7	Silicon	Upper part	5%	0.1%	Partially separated
8	Silicon	Upper part	2%	0.04%	Mostly separated (not attached)
9	Silica	Lower part	60%	1.2%	Good
10	Silica	Lower part	10%	0.2%	Good
11	Silica	Lower part	3%	0.06%	Mostly separated (not attached)

The magnesium composite powder in which the fine-grained powder was attached on the surface of the magnesium alloy coarse particle was provided by the wet granulating method using the PVA water solution as the binder. However, as shown in samples Nos. 7, 8 and 11, when the PVA solid quantity which remains on the powder surface as the binder was reduced, the fine-grained powder was not completely attached on the surface of the AZ31 coarse particle powder and a part or a most part thereof was separated from the surface, so that it was difficult to provide the predetermined magnesium composite powder.

(2) Working example 2

As a starting raw material to constitute a matrix to manufacture the magnesium alloy, AZ91 magnesium alloy coarse particle chip having a maximum particle diameter of 4.6mm, a minimum particle diameter of 680  $\mu\text{m}$  and an average particle diameter of 3.8mm and manufactured by cutting processing was prepared. Meanwhile, as the added powder, the silicon (Si) powder shown in the working example 1 was prepared.

The AZ91 coarse particle chip and the Si fine-grained powder were weighed so that 95% by weight of the AZ91 coarse particle chip and 5% by weight of the Si fine-grained powder might be provided. As a binder solution, the PVP (polyvinyl pyrrolidone) water solutions having concentrations shown in a table 3 were prepared to which the weighed Si fine-grained powder was mixed. In addition, 20% by weight of the PVP water solution was provided in the whole mixed powder.

[Table 3]

No.	PVP water solution concentration (%)	PVA solid quantity (%)	Attached state of Si fine-grained powder
1	4	0.8	Good
2	2	0.4	Good
3	1	0.2	Good
4	0.5	0.1	Partially separated
5	0.2	0.04	Mostly separated (not attached)
6	0 (Pure water)	0	Totally separated

The AZ91 alloy chip was put in the wet granulating machine and in a state where the AZ91 alloy chip was stirred by warm wind (kept at 75°C) from the lower part of the apparatus and the moving vane at the bottom of the apparatus, the PVP water solution comprising the above Si fine-grained powder was sprayed from the spray gun set at the lower part of the apparatus. At this time, the PVP water solution was sufficiently stirred by a screw while it was sprayed in order to prevent the Si powder from being precipitated in the PVP water solution.

There was provided magnesium composite powder in which the Si

fine-grained powder was attached on the surface of the AZ91 alloy chip using the PVP binder as a glue by spraying the PVP water solution containing the Si powder to the AZ91 alloy chip and drying it. Appearance result of attached states of the Si fine-grained powder on the AZ91 alloy chip surface provided under varied spraying conditions is shown in the table 3.

Thus, the magnesium composite powder in which the fine-grained powder was attached on the surface of the magnesium alloy coarse particle was provided by the wet granulating method in which the Si fine-grained powder was mixed in the PVP water solution previously and this was used as the binder. However, as shown in samples Nos. 4 and 5 in the table 3, when the PVA solid quantity which remains on the powder surface as the binder was reduced, the fine-grained powder was not completely attached on the surface of the AZ91 alloy chip and a part or a most part thereof was separated from the surface, so that it was difficult to provide the predetermined magnesium composite powder. In addition, when pure water which did not contain PVP was used, it was confirmed that the Si fine-grained powder could not be attached on the chip surface.

### (3) Working example 3

The AZ91 magnesium alloy coarse particle chip used in the working example 2 and the silica ( $\text{SiO}_2$ ) fine-grained powder shown in the working example 1 were prepared. The AZ91 coarse particle chip and the silica fine-grained powder were weighed and mixed so that 70% by weight of the coarse particle chip and 30% by weight of the silica fine-grained powder might be provided. The mixture was mechanically granulated using a vertical type of roller compactor. In addition, a roller had a configuration of a toothed wheel here. A speed of the roller at a peripheral part was set at 10mm/sec and a load between the toothed wheels was set at about 10Kgf. Result of appearance of provided granulated object observed by a scanning electronic microscope is shown in Fig. 13.

As shown in Fig. 13, the granules provided by the roller compactor were the magnesium composite powder in which the silica fine-grained powder was mechanically and uniformly attached on the AZ91 chip surface.

### (4) Working example 4

The AZ91 alloy chip used in the working example 2 and the alumina ( $\text{Al}_2\text{O}_3$ ) fine-grained powder shown in the working example 1 were prepared. The AZ91 coarse particle chip and the alumina fine-grained powder were weighed so that 96% by weight of the coarse particle chip and 4% by weight of the alumina fine-grained powder might be provided.

The AZ91 alloy chip to which the oleic oil was added was put in the ball mill together with steel balls (SUS2) having a diameter of 10mm and they were mixed for about 5 minutes. In this process, the oleic oil was uniformly attached on the chip surface.

Then, the above weighed alumina fine-grained powder was put in the ball mill and mixed for about 15 minutes again. Thus, there was provided magnesium composite powder in which the alumina fine-grained powder was attached on the AZ 91 chip surface.

Conditions of the added amount of the oleic oil to the AZ91 chip were changed as shown in a table 4. The appearance result of the attached states of the alumina fine-grained powder on the AZ91 alloy chip surface is shown in the table 4.

[Table 4]

No.	Addition amount of oleic oil (%)	Attached state of alumina fine-grained powder
1	3.0	Good
2	1.5	Good
3	0.5	Good
4	0.2	Partially separated
5	0 (No addition)	Mostly separated (not attached)

#### (5) Working example 5

Pure magnesium coarse particle powder having a maximum particle diameter of 1.8mm, a minimum particle diameter of 600 $\mu\text{m}$  and an average particle diameter of 920 $\mu\text{m}$  and the fine-grained powder of silicon (Si), silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and alumina (Al) used in the working example 1 were prepared.



Each powder was combined so that a chemical composition (percentage by weight) shown in a table 5 might be provided, and magnesium composite powder was manufactured by the vertical roller compactor used in the working example 3.

[Table 5]

No.	Chemical composition (percentage by weight)					Result of XRD of extruded material (detected phase)
	Si	SiO <sub>2</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	Al	Mg	
1	4	0	0	0	Balance	Mg <sub>2</sub> Si, Mg
2	0	3	0	0	Balance	Mg <sub>2</sub> Si, MgO, Mg,
3	0	0	3	0	Balance	MgO, Mg <sub>2</sub> Al <sub>3</sub> , Mg
4	0	0	0	5	Balance	Mg <sub>2</sub> Al <sub>3</sub> , Mg <sub>17</sub> Al <sub>12</sub> , Mg
5	2	0	2	0	Balance	Mg <sub>2</sub> Si, MgO, Mg <sub>2</sub> Al <sub>3</sub> , Mg
6	2	0	0	3	Balance	Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg <sub>17</sub> Al <sub>12</sub> , Mg
7	0	2	0	2	Balance	Mg <sub>2</sub> Si, MgO, Mg <sub>2</sub> Al <sub>3</sub> , Mg <sub>17</sub> Al <sub>12</sub> , Mg
8	4	0	0	0	Balance	Si, Mg
9	0	3	0	0	Balance	SiO <sub>2</sub> , Mg

A cylindrical pressed powder solidified body having a diameter of 36mm was manufactured by cold molding using each magnesium composite powder. Each solidified body was heated and held at 550°C for 5 minutes in a tube-shape furnace in which nitrogen gas flowed and then a warm extruding process was immediately performed at an extrusion ratio of 36, so that an extruded rod having a diameter of 6mm was provided.

In addition, when each pressed powder solidified body was heated to 700°C by a differential calorie analyzing apparatus, it was confirmed that an exothermic reaction caused by the generation of the compound had been completed at 550°C. X-ray diffraction (XRD) was performed on the extruded rods and generated compounds were identified. Its result is shown in the table 5.

As a reference, a result of the XRD to the magnesium alloys which were heated and held at 380°C which was lower than the exothermic reaction temperature by 100 to 150°C, for 5 minutes by the differential calorie analyzing apparatus and then provided by warm extrusion is shown as samples Nos. 8 and 9.

According to the magnesium alloys of samples Nos. 1 to 7, since the heating and holding temperature was low, the solid-phase reaction was not

progressed, so that the compound was not generated.

(6) Working example 6

Pure magnesium coarse particle powder used in the working example 5 and the  $\gamma$ -alumina ( $\text{Al}_2\text{O}_3$ ) used in the working example 1 and  $\alpha$ -alumina ( $\text{Al}_2\text{O}_3$ ) were prepared. Each powder was combined so that a chemical composition (percentage by weight) shown in a table 6 might be provided, and magnesium composite powder was manufactured by the vertical roller compactor used in the working example 3.

[Table 6]

No.	Chemical composition (percentage by weight)			Heating temperature (°C)	Result of XRD of extruded material
	$\gamma$ - $\text{Al}_2\text{O}_3$	$\alpha$ - $\text{Al}_2\text{O}_3$	Mg		
1	4	0	Balance	520	MgO, $\text{Mg}_2\text{Al}_3$ , Mg
2	4	0	Balance	580	MgO, $\text{Mg}_2\text{Al}_3$ , Mg
3	0	4	Balance	580	$\alpha$ - $\text{Al}_2\text{O}_3$ , Mg
4	0	4	Balance	645	$\alpha$ - $\text{Al}_2\text{O}_3$ , Mg

A cylindrical pressed powder solidified body having a diameter of 36mm was manufactured by cold molding using each magnesium composite powder. Each solidified body was heated and held at a temperature shown in the table 6 for 5 minutes in a tube-shaped furnace in which nitrogen gas flowed and then a warm extruding process was immediately performed at an extrusion ratio of 36, so that an extruded rod having a diameter of 6mm was provided. X-ray diffraction (XRD) was preformed on the extruded rods and generated compound phases were identified. Its result is shown in the table 6.

According to the magnesium alloys of samples Nos. 1 and 2, the added  $\gamma$ - $\text{Al}_2\text{O}_3$  fine-grained powder generated compound particles ( $\text{MgO}$  and  $\text{Mg}_2\text{Al}_3$ ) by the solid-phase reaction with the pure magnesium coarse particle powder in the course of heating and holding process at 520°C and 580°C.

Meanwhile, according to the magnesium alloys of the samples Nos. 3

and 4, even when they were heated and held at 645°C which was close to a melting point of magnesium,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder did not react with the magnesium coarse particle powder, so that a compound was not generated.

(7) Working example 7

The AZ31 alloy coarse particle powder used in the working example 1 was prepared as magnesium alloy base powder, and silicon (Si) fine-grained powder having particle diameters shown in a table 7 were prepared as the powder to be added. Magnesium composite powder comprising the AZ31 alloy coarse particles and the Si fine-grained powder was manufactured so as to contain 4% by weight of the Si powder.

[Table 7]

No.	Particle diameter of Si powder (μm)			Tensile characteristics of extruded material at room temperature		Others
	Maximum	Average	Minimum	Tensile strength (Mpa)	Breaking elongation (%)	
1	78	26	5	315	3.9	
2	68	17	4	322	4.3	
3	37	11	2	345	6.7	
4	24	8	1	356	7.3	
5	8	4	0.7	359	9.9	
6	167	109	54	268	2.4	Fine-grained powder is aggregated
7	4	2	0.2	288	2.7	

In addition, the composite powder was manufactured in such a manner that oleic oil was applied to the AZ31 coarse particle and then Si powder was attached on the surface of the AZ31 coarse particle powder using a ball mill by the method shown in the working example 4.

A cylindrical pressed powder solidified body having a diameter of 36mm was manufactured using each magnesium composite powder. Each solidified body was heated and held at 550°C for 5 minutes in a tube-shaped furnace in which nitrogen gas flowed and then a warm extruding process

was immediately performed at an extrusion ratio of 36, so that an extruded rod having a diameter of 6mm was provided. In addition, X-ray diffraction was performed on the extruded magnesium alloys. As a result, it was confirmed that  $Mg_2Si$  particles were generated by the solid-phase reaction in any case.

A tensile specimen was extracted from each extruded material by mechanical processing and a tensile test was performed at room temperature. Its result is shown in the table 7.

According to the magnesium alloys of the sample Nos. 1 to 5, particle diameters of the Si powder to be added satisfied the above appropriate range and as the particle diameter becomes small, the tensile strength of the magnesium alloy provided by the extruding process was improved. In addition, when the Si particle diameter was not more than  $50\mu m$ , an increase in elongation was recognized in addition to the strength, and when the Si fine-grained powder having a particle diameter of  $10\mu m$  or less is used, the breaking elongation of the magnesium alloy was considerably improved.

Meanwhile, according to the sample No. 6, since the Si powder having a particle diameter beyond  $100\mu m$  was used, the tensile strength and the breaking elongation of the magnesium alloy were lowered.

According to the sample No.7, since Si powder having a fine particle diameter below  $0.5\mu m$  was used, a composition in which large  $Mg_2Si$  was dispersed in the matrix of the magnesium alloy was formed by an aggregation phenomenon of the fine particles. As a result, the tensile strength and the breaking elongation of the magnesium alloy were lowered.

#### (8) Working example 8

The AZ31 coarse particle powder and the silica ( $SiO_2$ ) fine-grained powder used in the working example 1 were prepared. In addition, graphite powder having an average particle diameter of  $3\mu m$  was used in the starting material as a solid lubrication component. Compounding

ratios of the powder are shown in a table 8.

[Table 8]

No.	Chemical composition (percentage by weight)			Identified phase by XRD	Average friction coefficient ( $\mu$ )	Tensile strength of extruded material (MPa)
	Silica	Graphite	AZ31			
1	3	0	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.035	344
2	3	0.5	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.014	320
3	3	1.0	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.012	312
4	3	2.0	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.011	306
5	3	3.0	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.010	302
6	3	3.5	Balance	MgO, Mg <sub>2</sub> Si, Mg <sub>2</sub> Al <sub>3</sub> , Mg	0.058	268

According to a method of attaching the silica powder and the graphite powder on the surface of the AZ31 coarse particle surface, similar to the wet granulating method shown in the working example 2, the silica powder and the graphite powder were previously added in the 2% PVA water solution, and the PVA water solution was applied to the AZ31 coarse particle surface from a lower part of the granulating apparatus through a spray gun to manufacture magnesium composite powder.

A cylindrical pressed powder solidified body having a diameter of 40mm was manufactured using each magnesium composite powder. Each solidified body was heated and held at 550°C for 5 minutes in a tube-shaped furnace in which nitrogen gas flowed and then a warm extruding process was immediately performed at an extrusion ratio of 25, so that an extruded rod having a diameter of 8mm was provided. X-ray diffraction was performed on each extruded magnesium alloy. As a result, it was confirmed that Mg<sub>2</sub>Si particles were generated by the solid-phase reaction in any case.

In order to measure a friction coefficient by a rubbing test, a pin-shaped abrasion test specimen (whose diameter is 7.8mm) was extracted from the extruded material. As an opponent disk material, C35C steel material was used, and a pressing load, a sliding velocity and a testing time were set at 500N, 1m/s and 30minutes in a row, respectively. In

addition, engine lubrication oil (10W30) was dropped from an upper part of the pin-shaped test specimen and the test was performed under a wet lubrication condition in which the lubrication oil existed always on the sliding interface between the pin-shaped test specimen and the disk test specimen. The result of the friction coefficients calculated from the measured friction torque is shown in the table 8.

According to the samples Nos. 1 to 5, since the tensile strength of the magnesium alloys were slightly lowered as the content of the graphite powder is increased, but friction coefficients could be largely reduced.

Meanwhile, according to the sample No. 6, since the graphite amount was beyond the appropriate range, the tensile strength of the extruded material was considerably lowered. As a result, since an adhesion phenomenon with the opponent material was induced in the course of the rubbing test because of the abrasion damage of the pin-shaped test specimen, the friction coefficient was increased.

#### (9) Working example 9

The AZ31 alloy coarse particle powder used in the working example 1 was prepared as a magnesium alloy matrix. Meanwhile, as the added powder, the silicon (Si) fine-grained powder (its maximum particle diameter was 24 $\mu$ m, average particle diameter was 8 $\mu$ m and minimum particle diameter was 1 $\mu$ m) was prepared. Magnesium composite powder comprising the AZ31 alloy coarse particle and the Si fine-grained powder was manufactured so that the combined composition might become AZ31-4%Si by weight.

In addition, the composite powder was manufactured in such a manner that oleic oil was applied to the AZ31 coarse particle previously and then the Si powder was attached on the surface of the AZ31 coarse particle powder by a ball mill by the method shown in the working example 4. In addition, 0.3% by weight of the oleic oil was added in the AZ31 alloy powder. At this time, the Si powder was uniformly attached on the surface of the AZ31 coarse particle in the obtained composite powder, and the Si powder was not separated from the surface and the attached state was preferable. A cylindrical pressed powder solidified body (whose relative density was

91%) having a diameter of 36mm was manufactured using each magnesium composite powder and heated and held at 550°C for 5 minutes in a tube-shaped furnace in which nitrogen gas flowed and then the warm extruding process was immediately performed on the solidified body to provide an extruded rod.

It was set that the extrusion ratio  $R = \text{a square of (diameter of molded solidified body/diameter of extruded material)}$  and the extrusion ratios used here are shown in a table 9. Then, the X-ray diffraction was performed on each extruded magnesium alloy and it was confirmed that the  $\text{Mg}_2\text{Si}$  particles were generated by the solid-phase reaction in any case.

A tensile test specimen was extracted from each extruded material by mechanical processing and a tensile test was performed at room temperature and its result is shown in a table 9.



[Table 9]

No.	Extrusion ratio R	Tensile characteristics of extruded material at room temperature	
		Tensile strength (Mpa )	Breaking elongation (%)
1	48	361	7.1
2	36	356	7.3
3	27	342	5.8
4	21	334	5.2
5	16	305	3.3

When the extrusion ratio was not less than 20, as the value of the extrusion ratio was increased, the tensile strength and the breaking elongation of the extruded material were both increased and when it exceeds 35, their mechanical characteristics were considerably improved. Meanwhile, when the extrusion ratio was below 20 like the sample No. 5, the tensile strength and the breaking elongation of the extruded material were lowered.

#### (10) Working example 10

The AZ31 alloy coarse particle powder and the silicon powder used in the working example 9 were prepared and both were weighed so that the combined composition might become AZ31-4%Si by weight. To manufacture composite powder, the AZ31 coarse particle powder was put in a cylindrical vinyl container and 0.1%, 0.25% and 0.4% by weight of oleic oil were added to it and the container was rotated and shaken for 15 minutes. Then, the Si powder was put in the container and they were mixed by rotating and shaking the container for 15 minutes to manufacture three kinds of predetermined magnesium composite powder.

Fig. 14 shows a method to evaluate an attached state of the silicon powder easily. The evaluation of the attached state was made as follows.

- 1) The composite powder is put and spread on white paper.
- 2) The powder is slid downward with the paper tilted.
- 3) The paper is set up vertically to drop off the composite powder completely. At this time, the paper should not be patted because the Si powder remaining on the paper would come off.
- 4) An attached state of the Si powder remaining on the paper is observed.

Fig. 15 shows the result of the attached states of the silicon powder.

According to cases where (a) 0.25% by weight of the oleic oil was used and (b) 0.4% by weight of the oleic oil was used, since almost no Si powder was remained on the white paper, it was recognized that the Si powder was strongly attached on the surface of the AZ31 alloy coarse particle. Meanwhile, according to a case where (c) 0.1% by weight of the oleic oil was used, which is a comparison example, since the Si powder was mostly remained on the white paper, it was recognized that the Si powder was separated without being attached on the surface of the AZ31 coarse particle powder.

#### INDUSTRIAL APPLICABILITY

The present invention can be applied to a component for an automobile, a bicycle, a bike, a mechanical component, a structural component, an industrial robot arm, a medical instrument, a nursing-care assistance device, a baby carriage component and the like.